SEGMENTED LEAD TELLURIDE - SILICON GERMANIUM THERMOELEMENTS

by

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The segmenting of various thermoelectric materials has long been hypothesized as a method for increasing the efficiency and utility of thermoelectric energy conversion systems. The ability to couple the best attributes of two or more materials over an extended temperature range can provide a significant increase in thermal utilization and result in a high overall efficiency and specific power. This is especially important in space power systems dependent upon radioisotope decay as a thermal energy source. High efficiency and specific power are directly related to low system weights and fuel inventories; and indirectly related to reliability and lifetime by providing the means for achieving redundancy, derating and margins of safety at reduced system weight penalties.

The thermoelectric materials of current interest for space power systems seem to be limited to lead telluride (Pb Te) and silicon germanium (Si Ge). Each of these materials has been segmented with some success to various other materials: Lead telluride with other tellurides; and silicon germanium with some of the III-V compounds and with doped carbides. The two materials of basic interest have not been previously joined to form an integral thermoelement in spite of the excellent temperature regime coupling that may be achieved, Figures 1 and 2. A comparison of optimum efficiencies that may result from the application of the more useful thermoelectric materials in the segmented and unsegmented forms is shown in Figures 3 and 4 for terrestrial and space systems. Practicable cold junction temperatures of 50°C and 200°C, respectively, have been chosen based on available cooling water temperatures at 25°C and optimum space radiator temperatures at 175°C. It is obvious that the greatest advantage may be gained by segmenting Pb Te with Si Ge. There is, however, an obvious mismatch in thermal expansion:

$$\text{Si Ge} \approx 2 \times 10^{-6} \, (^\circ\text{F})^{-1}$$
$$\text{Pb Te} \approx 10 \times 10^{-6} \, (^\circ\text{F})^{-1},$$

which has formerly been cited to emphasize the futility of attempting the direct segmentation of the two materials.

A recent study[1] investigating the bonding of thermoelectric materials to non-magnetic electrodes has shown that it is not only possible to bond both "n" and "p" type Pb Te directly to tungsten (W) electrodes, but that the process is a

comparatively simple and inexpensive one. The replacement of the W-electrodes by commercially available W-bonded Si Ge elements became a distinct possibility and a few segmented elements were fabricated for preliminary studies and evaluation.

The process used for segmenting the Pb Te and W-bonded Si Ge elements is essentially the same as that reported[2] for W-bonded Pb Te. The plated surface is removed from the bonded Si Ge electrode to expose the bare tungsten surface. The surfaces to be joined are lapped, cleaned, heated in carbon jigs to 850°C, and then allowed to cool slowly (< 6°C/min). A study[2] of the process variables involved in preparing the W-bonded elements indicated that flatness of the adjacent surfaces was considerably more important than surface finish; and that pressure and time at temperature did not adversely affect bonding or reproducibility.

The segmented elements fabricated were commercially sized Pb Te (MMM-3N) and $Pb_{0.5}$ $Sn_{0.5}$ Te (MMM-3P), 1.11 cm in diameter and 0.635 cm in length. The "n" and "p" type Si Ge elements were 0.79 cm in length with 1 mm W-electrodes. The interface electrode was 0.5 mm after removal of the surface plating. A 3 mil chromel-alumel thermocouple was spot welded to the interface electrode. The hot and cold junction temperatures were measured with chromel-alumel thermocouples that were spring loaded at the ends of the element. Electrical measurements were made with pure nickel lead wires soldered into slots on the cold side of the Pb Te and spot welded to the hot junction W-electrode of the Si Ge.

The results of the electrical measurements for the few elements prepared are shown in Figure 5 as a function of hot junction temperature to 800°C. The variation of interface electrode temperature is shown in Figure 6. The experimentally obtained values of open circuit voltage and resistance for "n" and "p" elements operating over the temperature difference 115°C to 800°C indicate an efficiency greater than 11%, and a power output to a matched load of 2.7 watts at 0.15 volts per couple. A volt-ampere characteristic curve for a segmented couple operating over the temperature difference 28°C to 585°C is shown in Figure 7. The segmented elements fabricated were not optimized for either peak efficiency or maximum power and it therefore seems possible to achieve an additional two percent in efficiency by the simple expedient of using consistent area to length ratios for each segment of the element over its respective optimum operating temperature range.

The changes in thermoelectric properties and contact resistivity due to the W-bond to Pb Te is the most critical of the areas involved in producing segmented elements and couples. Several hundreds of test hours accumulated at 600°C

does not seem to result in any significant change in the electrical properties of the W-bonded elements. A comparison of the electrical properties for "n" and "p" type W-bonded Pb Te is shown in Figures 8 and 9.

Measurements of the contact resistance for several "p" type W-bonded Pb Te elements resulted in an average value of $60\mu\Omega$ ($20\mu\Omega$-cms^2). The "n" type material measurements were somewhat better ($5\mu\Omega$-cm^2). These values are room temperature values and if extrapolated to hot junction temperatures using the relationship postulated by Jain and Barry[3] and verified for this system by Weinstein and Bates[4]:

$$p_c \propto T^x$$

where;

p_c = contact resistivity
T = hot junction temperature
x = a constant, 2.5

then;

at 500°C, a room temperature contact resistivity of $5\mu\Omega$-cms^2 would be equivalent to about 0.2 mΩ for an element 0.635 cm in diameter. Contact resistivity is also a time dependent value and it is therefore difficult to assess its contribution to system degradation without long term test data. The values reported here are less than usually measured for braze bonded Pb Te elements.

The nature and mechanism of the bond is unknown at present but electron microprobe studies indicate that there is neither compound formation nor diffusion to within the limit of the probe size, 3 microns. Elements microprobed after 500 hrs at 600°C show no broadening of the interface due to diffusion or compound formation. Figure 10 is a backscatter photograph with superimposed microprobe trace for a W-bonded Pb Te n-type element. The grid size is 5 microns.

Substantial progress has already been made in fabricating and testing segmented Pb Te - Si Ge thermoelectric elements. Much work remains to be done before their practicable application becomes a reality. The nature and mechanism of the bond must be explored and understood; long term, > 10,000 hrs of operation, must be achieved; methods for preparing couples and modules of segmented elements must be examined; and analytical and experimental work in device design using segmented elements must be initiated. At this point it does not seem unreasonable to assume that thermoelectric power sources with two to three times the efficiency of present day systems will be available within a few years.

REFERENCES

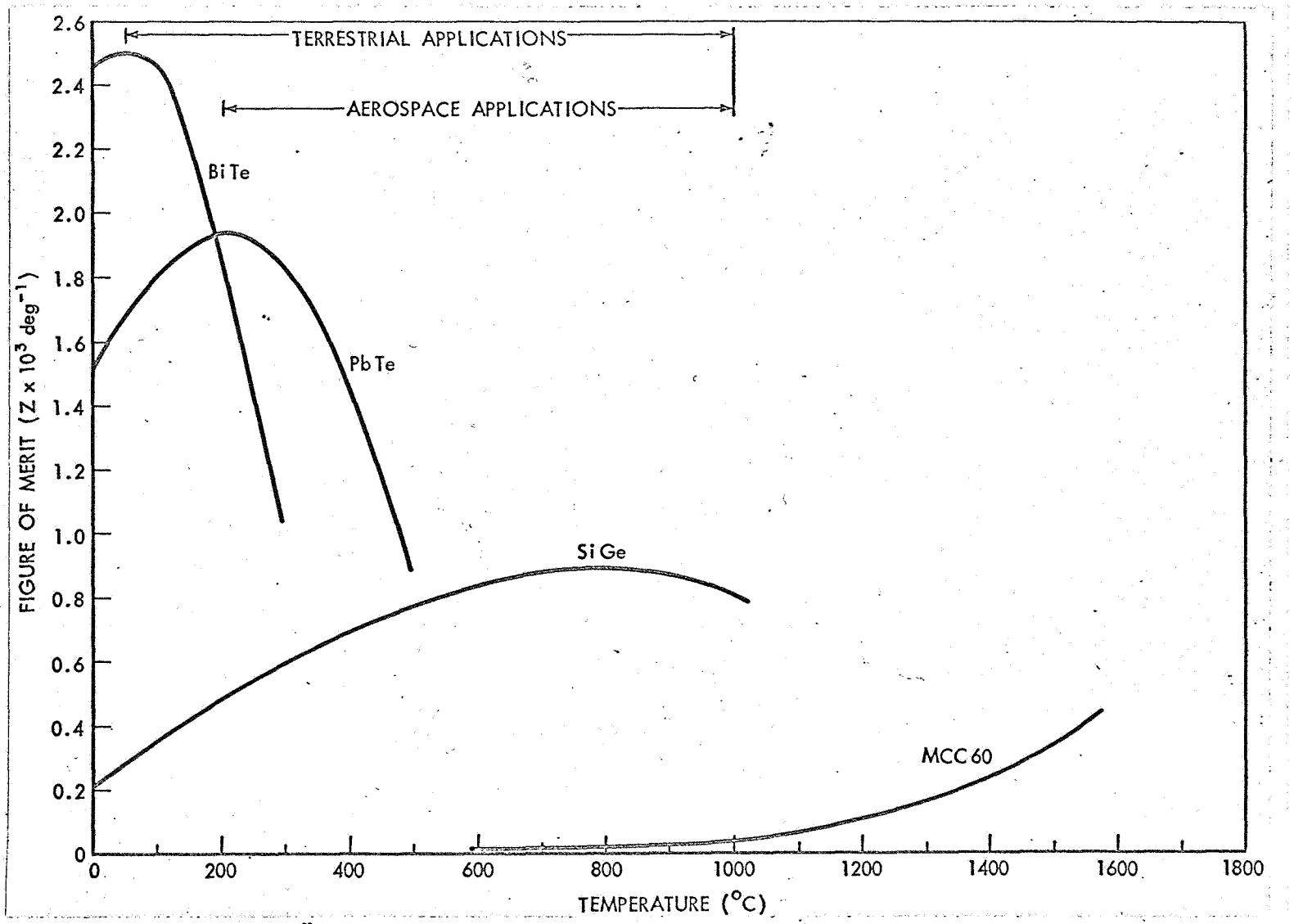
1. Weinstein, M. and H. E. Bates, Technical Summary Report-Thermoelectric Bonding Study, (January, 1965), contract NAS 5-3986, Tyco Laboratories, Inc., Waltham, Massachusetts; also NASA CR-290.

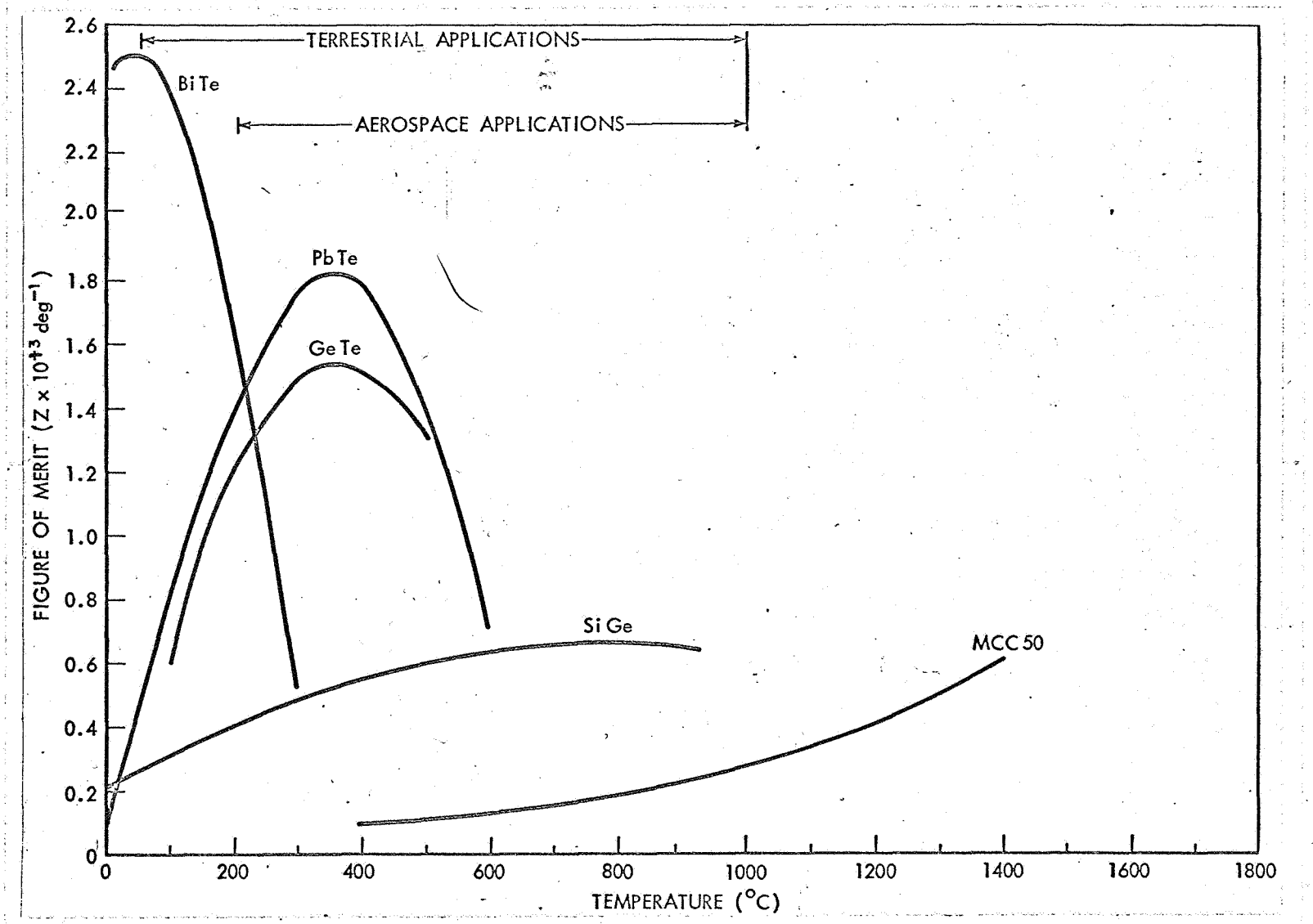
2. Weinstein, M. and H. E. Bates, First Quarterly Report - Lead Telluride Non-Magnetic Bonding Research Study, (May, 1965), contract NAS 5-9149, Tyco Laboratories, Inc., Waltham, Massachusetts.

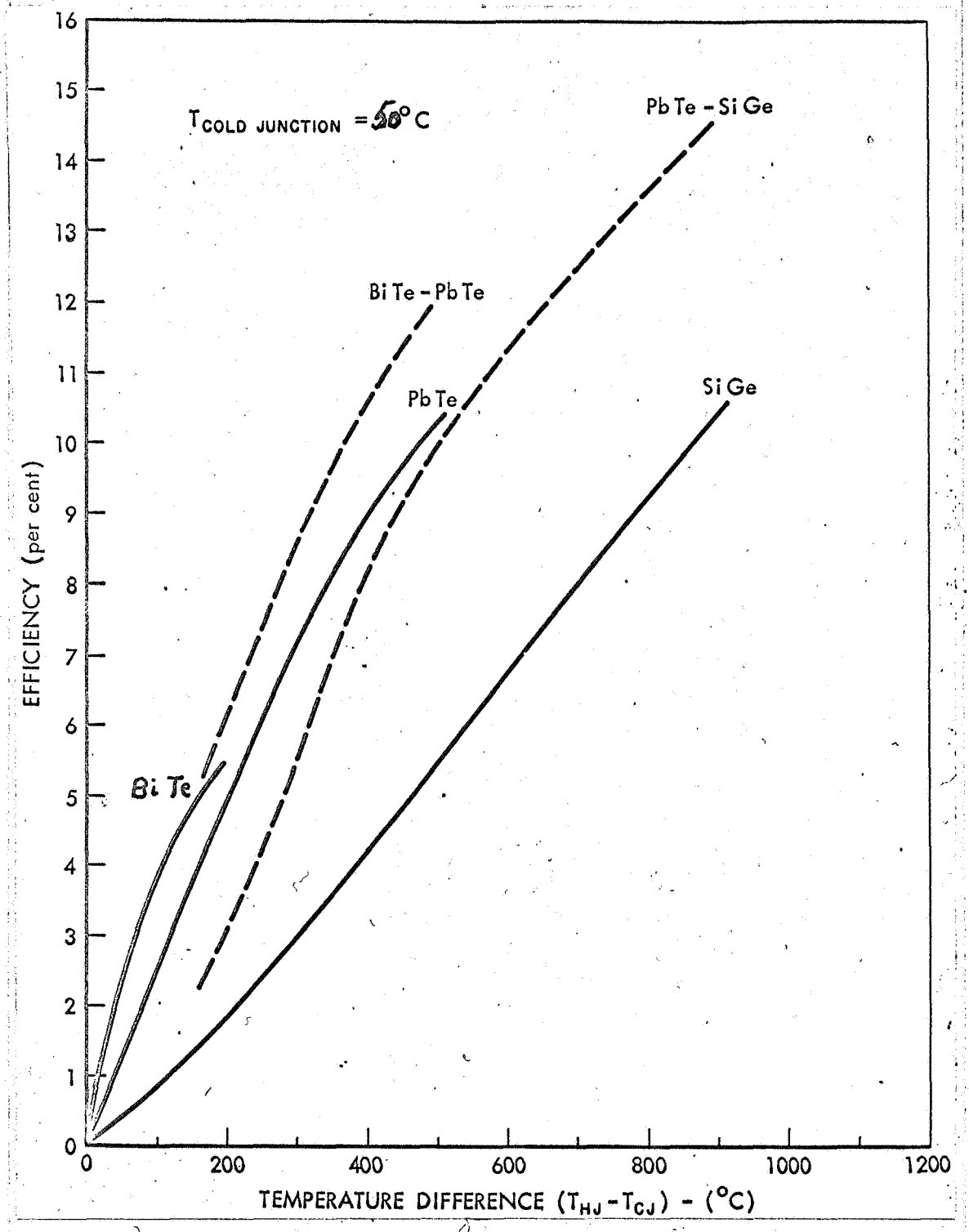
3. Jain, G. C. and W. B. Barry, Advanced Energy Conversion, 4, 159 (1964).

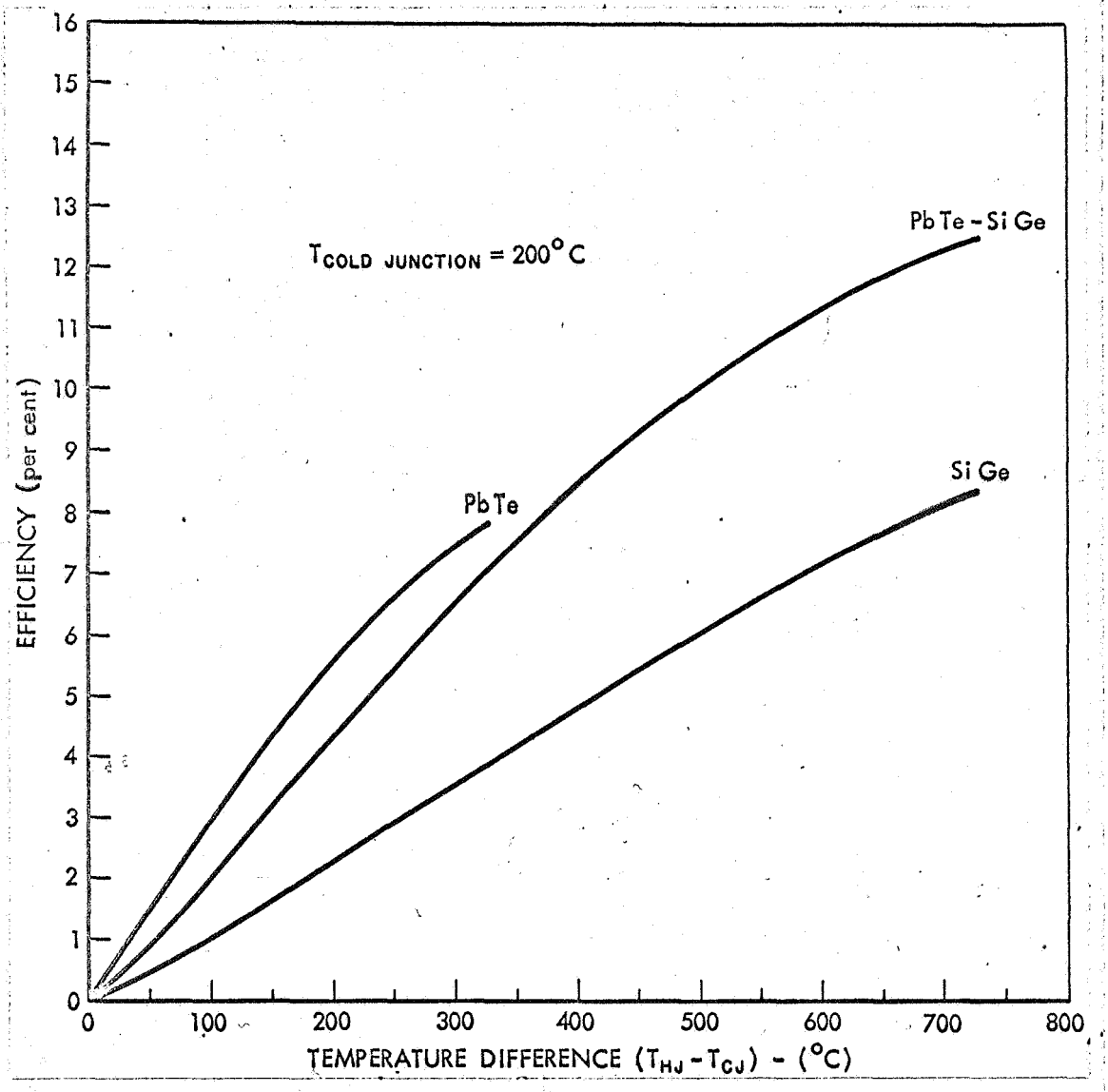
4. Weinstein, M., and H. E. Bates, The Bonding of Lead Telluride With Non-Magnetic Electrodes, AIAA/IEEE Thermoelectric Specialists Conference, May 17 - 19, 1966, Washington, D. C.

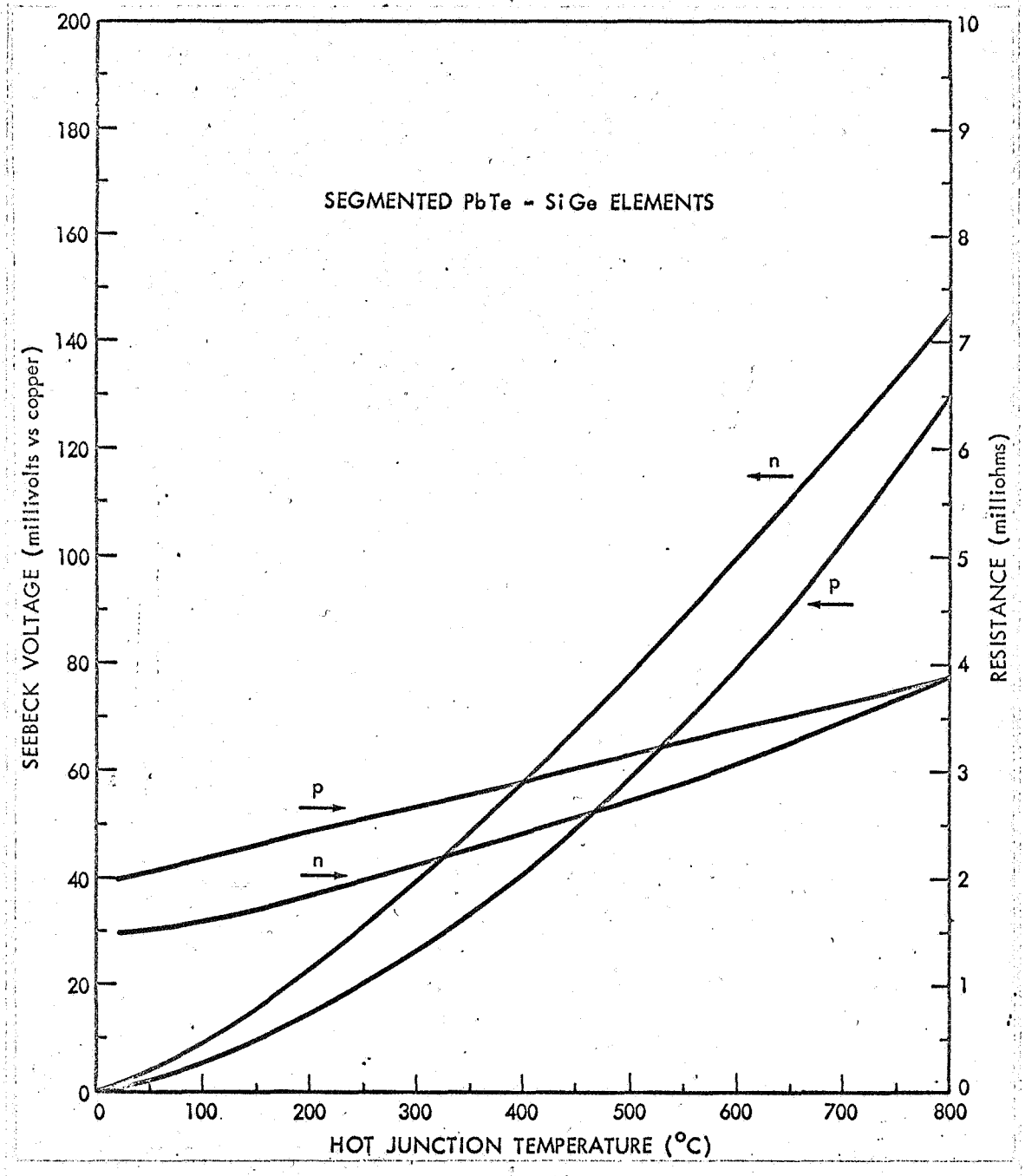
LIST OF ILLUSTRATIONS

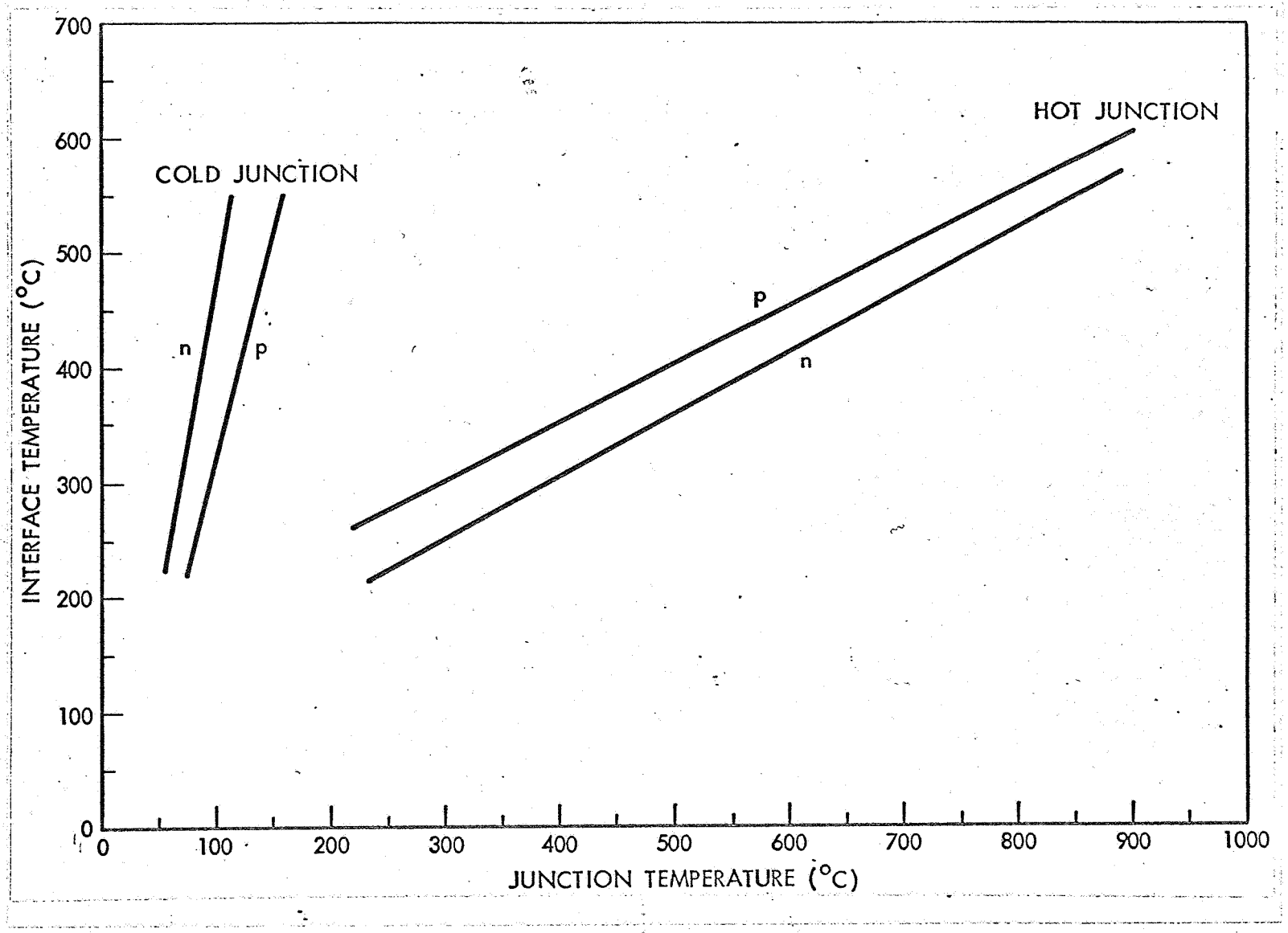

TERRESTRIAL APPLICATIONS
AEROSPACE APPLICATIONS
Bi Te
Pb Te
Si Ge
MCC 60
FIGURE OF MERIT (Z x 10³ deg⁻¹)
TEMPERATURE (°C)
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000
1200
1400
1600
1800

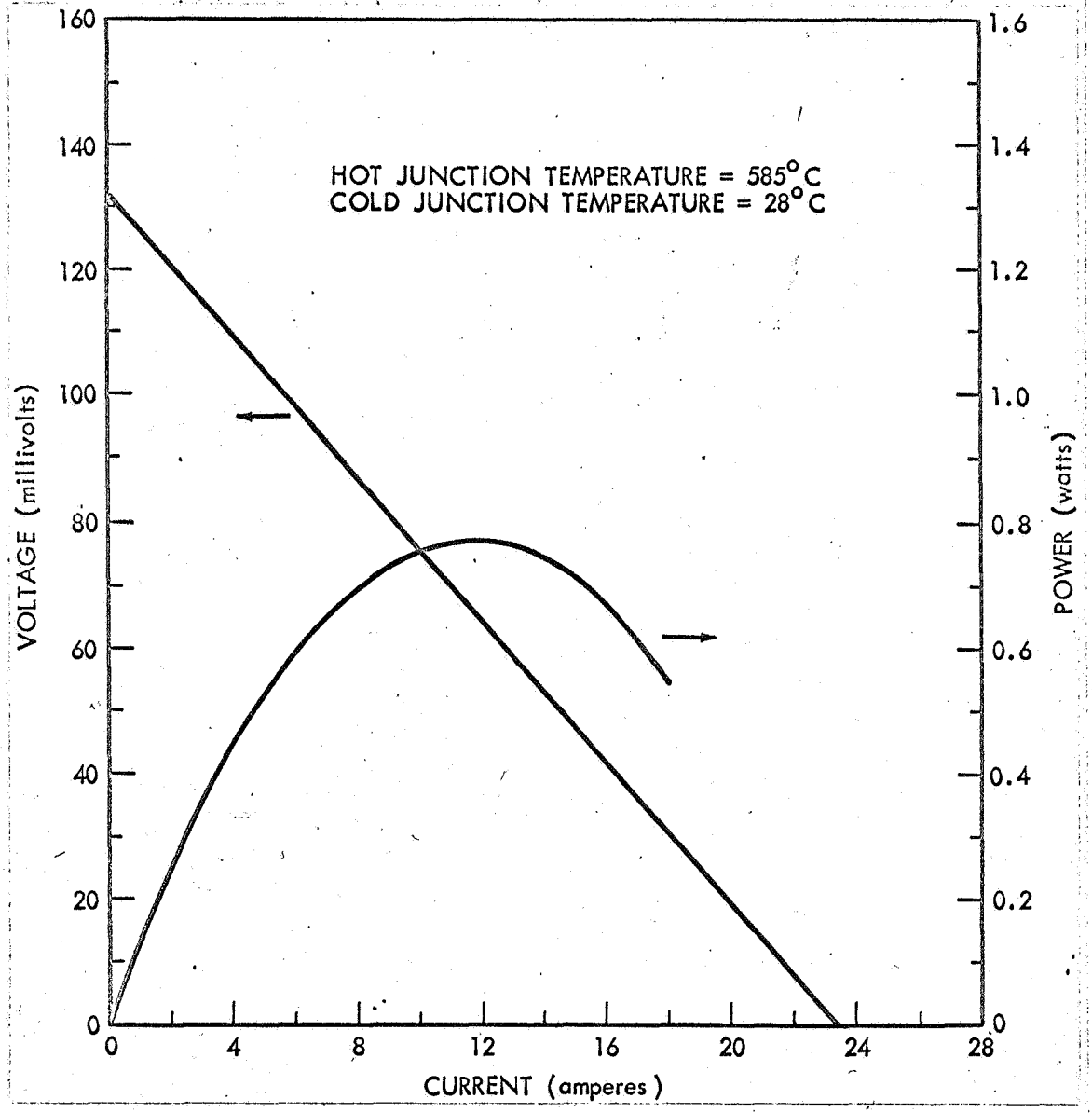

TERRESTRIAL APPLICATIONS
AEROSPACE APPLICATIONS
Bi Te
Pb Te
Ge Te
Si Ge
MCC 50
FIGURE OF MERIT (Z x 10+3 deg-1)
TEMPERATURE (°C)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
0
200
400
600
800
1000
1200
1400
1600
1800

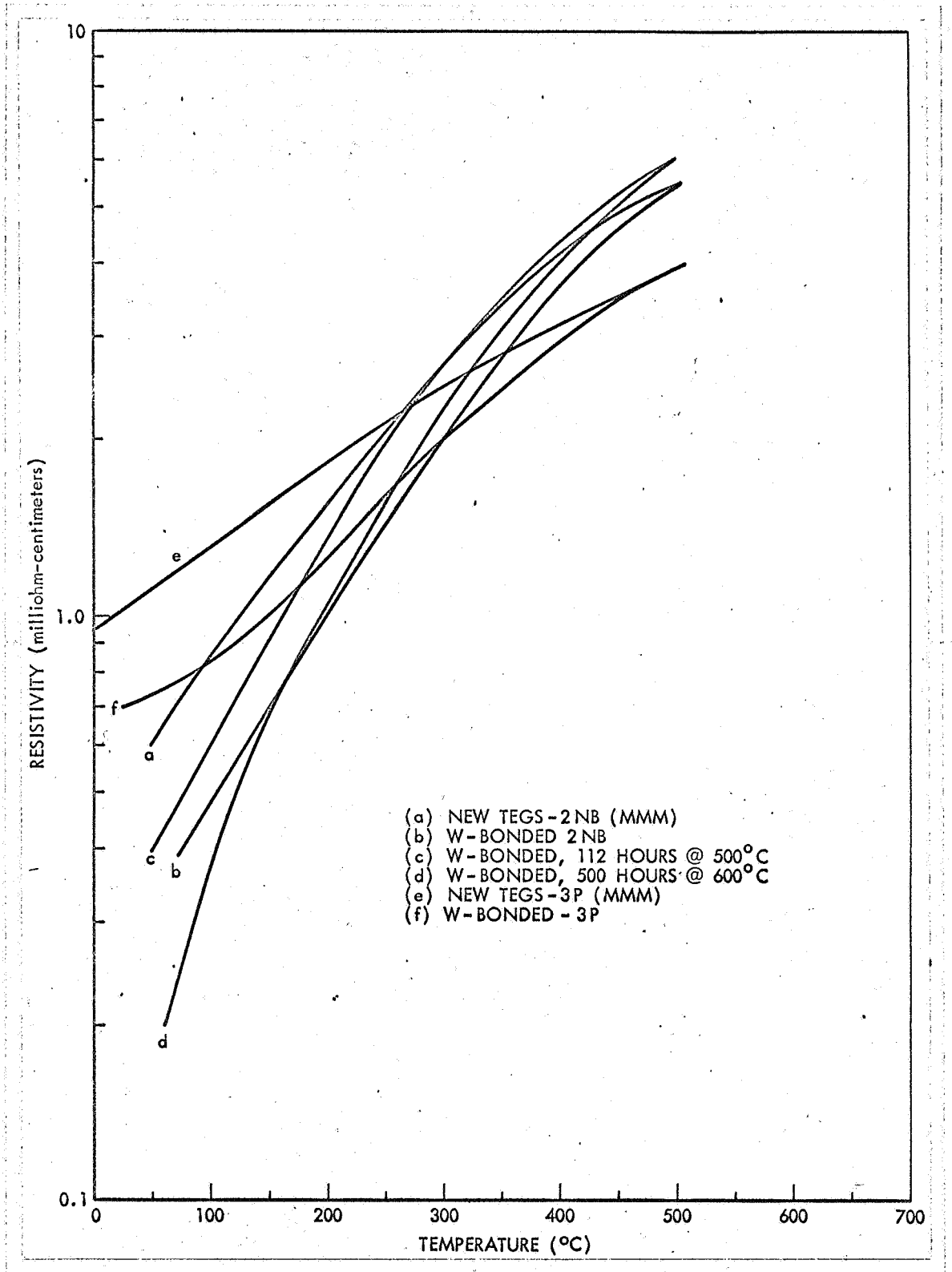

T COLD JUNCTION = 50° C
Pb Te - Si Ge
Bi Te - Pb Te
Pb Te
Si Ge
Bi Te
EFFICIENCY (per cent)
TEMPERATURE DIFFERENCE (T_HJ - T_CJ) - (°C)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0
200
400
600
800
1000
1200

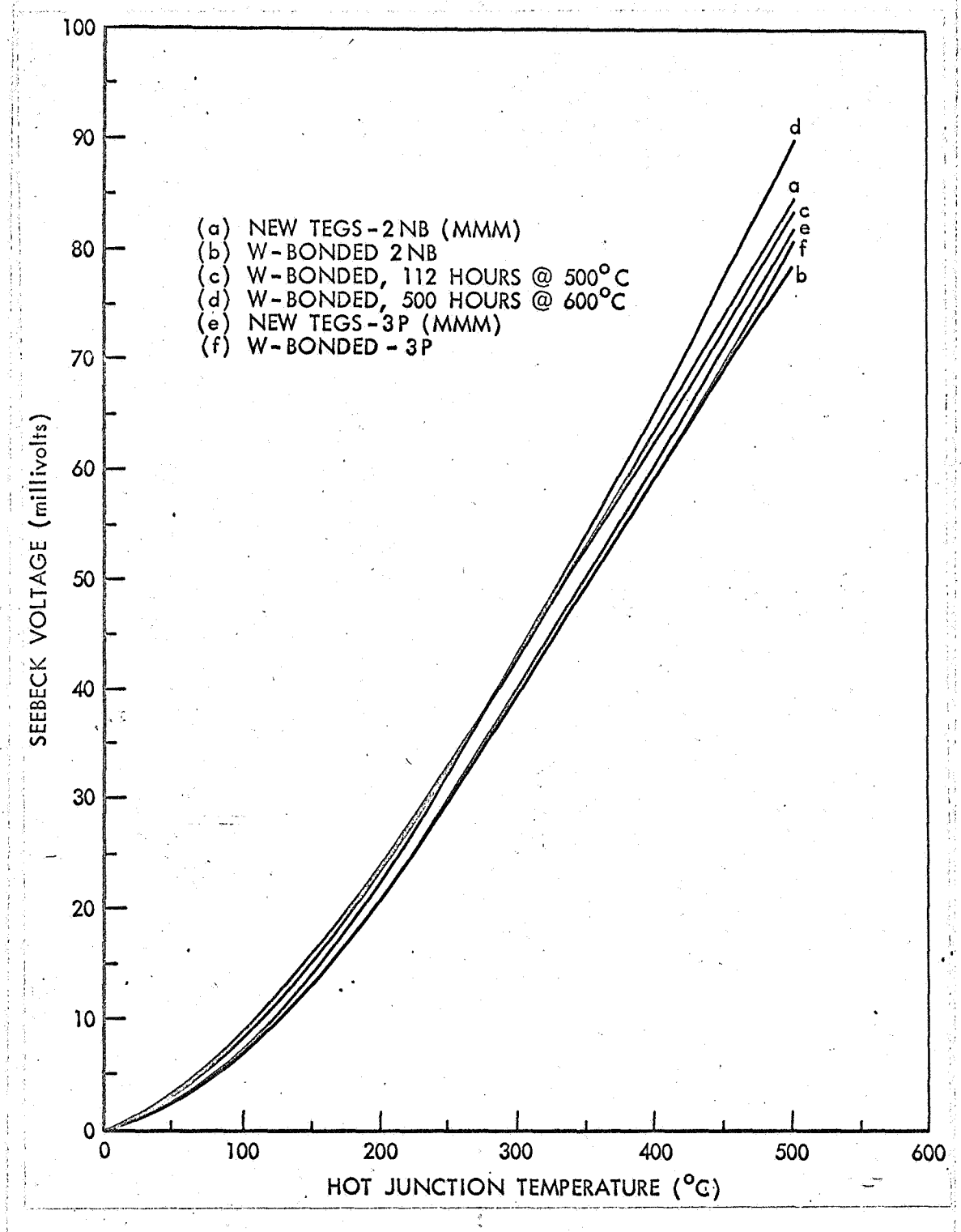

EFFICIENCY (per cent)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
$T_{COLD\ JUNCTION} = 200^{\circ}C$
Pb Te - Si Ge
Pb Te
Si Ge
0
100
200
300
400
500
600
700
800
TEMPERATURE DIFFERENCE ($T_{HJ} - T_{CJ}$) - (°C)

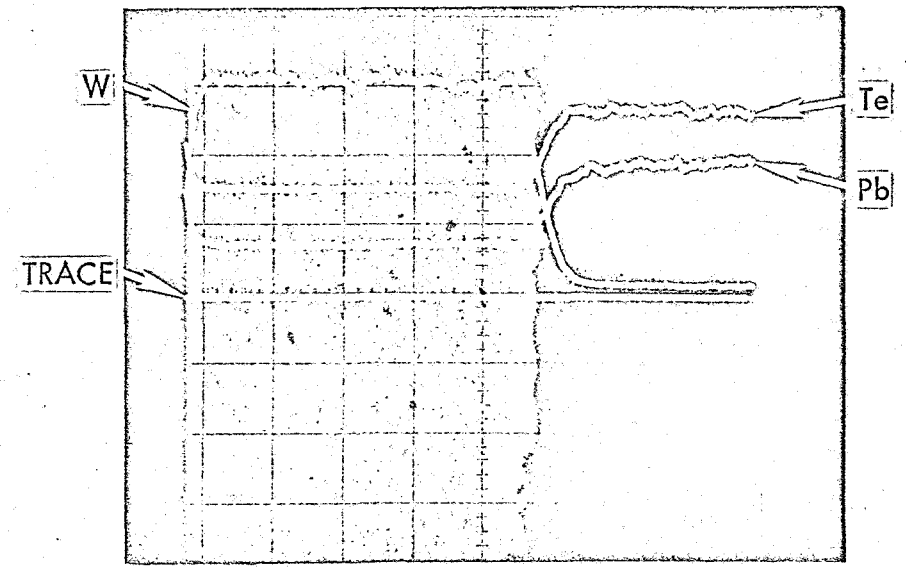

SEGMENTED PbTe - SiGe ELEMENTS
SEEBECK VOLTAGE (millivolts vs copper)
RESISTANCE (milliohms)
HOT JUNCTION TEMPERATURE (°C)
200
180
160
140
120
100
80
60
40
20
0
10
9
8
7
6
5
4
3
2
1
0
0
100
200
300
400
500
600
700
800
n
p
p
n


HOT JUNCTION
COLD JUNCTION
p
n
n
p
INTERFACE TEMPERATURE (°C)
JUNCTION TEMPERATURE (°C)
0
100
200
300
400
500
600
700
800
900
1000


HOT JUNCTION TEMPERATURE = 585°C
COLD JUNCTION TEMPERATURE = 28°C
VOLTAGE (millivolts)
POWER (watts)
CURRENT (amperes)
160
140
120
100
80
60
40
20
0
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
4
8
12
16
20
24
28


10
1.0
0.1
RESISTIVITY (milliohm-centimeters)
0
100
200
300
400
500
600
700
TEMPERATURE (°C)
a
b
c
d
e
f
(a) NEW TEGS-2NB (MMM)
(b) W-BONDED 2NB
(c) W-BONDED, 112 HOURS @ 500°C
(d) W-BONDED, 500 HOURS @ 600°C
(e) NEW TEGS-3P (MMM)
(f) W-BONDED - 3P


(a) NEW TEGS-2NB (MMM)
(b) W-BONDED 2NB
(c) W-BONDED, 112 HOURS @ 500°C
(d) W-BONDED, 500 HOURS @ 600°C
(e) NEW TEGS-3P (MMM)
(f) W-BONDED - 3P
SEEBECK VOLTAGE (millivolts)
HOT JUNCTION TEMPERATURE (°C)
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
a
b
c
d
e
f


W
TRACE
Te
Pb